

Preparation of phenol formaldehyde resin from phenolated wood

LI Gai-yun¹, QIN Te-fu¹, Tohmura Shin-ichiro², Ikeda Atsushi³

¹ Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing 100091, P. R. China

² Department of Wood Composite Materials, Forestry and Forest Products Research Institute, Tsukuba 305-8687, JAPAN

³ Expert of Research Project on Man-Made Forestry Timber Dispatched by Japan International Cooperation Agency

Abstract: The technique for preparing phenol formaldehyde resin from phenolated wood (PWF) and its characters were studied and analyzed. Poplar (*Populus spp.*) wood meal was liquefied by phenol in the presence of sulfuric acid as a catalyst. After the liquefied products were cooled, alkaline catalyst and formaldehyde were added. The mixture was kept at (60±2) °C for 1h and then was heated to (85±2) °C for 1h. The influence of molar ratio of formaldehyde to phenol (F/P) was investigated. The results showed when the molar ratio of formaldehyde to phenol was over 1.8, the PWF adhesives had high bond quality, bond durability and extremely low aldehydes emissions.

Keywords: Phenolated wood; Phenol formaldehyde (PF) adhesives; Bond quality; Bond durability; Aldehyde emission.

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Introduction

Wood liquefaction is one of the promising approaches to utilize lignocellulosic biomass. By means of liquefaction, the wood wastes and other renewable woody biomass resources can be converted into useful chemical intermediates, which have been used as raw materials of adhesives (Lin *et al.* 1995; Maldas *et al.* 1997; Marcos *et al.* 1996; Shiraishi *et al.* 1986), foams (Yao *et al.* 1995; Alma *et al.* 1998), fibers, and carbon fibers (Tsujiimoto 1984; Shiraishi *et al.* 1993), etc.

The liquefaction of lignocellulosic biomass and the properties of the resulting liquefied materials have been extensively investigated in Japan. It was reported that different wood species showed the influence on the liquefaction (Kurimoto *et al.* 1999). However, the study on wood liquefaction was carried out by using only a specific wood species such as Japanese birch. On the other hand, the weight ratio of liquefaction solvent to wood ranges from 2.5 to 5. Therefore, the large amount of liquefaction solvent leads to increase the cost of liquefied wood products and caused suspicion from environmental protectionism.

In this study, the liquefaction of poplar with phenol was investigated in order to learn the properties of liquefied Chinese plantation wood and the application field of liquefied wood products. The weight ratio of wood to liquefaction solvent was improved to 0.7. The application of liquefied wood products to PF adhesive was studied.

Materials and methods

Materials

Wood meal used in the study was of 20-80 mesh from Poplar. Phenol, sulfuric acid, sodium hydroxide, formaldehyde solution (36wt%) and sodium hydrogen carbonate were of guaranteed reagents. N, N-dimethylformamide (DMF) is of HPLC grade reagent. Other materials were obtained from commercial sources.

Preparation of phenolated wood

The phenolation reaction of wood was conducted in reaction container equipped with a stirrer and a temperature controller. Wood meal, phenol and acid catalyst (The weight ratio of wood and Phenol to Sulfuric acid was 0.7:1:0.05) were premixed well, then at 150 °C for 90 min. The products were neutralized by using a predetermined amount of sodium hydroxide after cooling.

Determination of free phenol

The amounts of free phenol in the liquefied products were determined on a high performance liquid chromatograph (HPLC, Shimadzu LC-10A) equipped with a UV detector (Shimadzu SPD-10Avp) and a column (Inertsil ODS-3). The binary gradient elution with water and methanol was used. The flowing rate of the eluent was 1 mL/min. The amount of free phenol (%) in the liquefied product was determined to be 10.15%.

Determination of molecular weight

The molecular weight of the liquefied product was determined on a gel permeation chromatography (GPC, Shimadzu LC-6A) equipped with two GPC columns (Shodex GPC KD-806M and KD-802 in series). DMF (N, N-dimethylformamide) mixed with 0.01M of LiBr was used

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Biography: LI Gai-yun (1974-), female, Assistant professor in Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing 100091, P. R. China (E-mail: ligy@forestry.ac.cn).

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as the eluent at the flow rate of 1 mL/min. The chromatograms were recorded with a refractometer. The concentration of the sample in eluent was 0.5%-1%, and the injecting amount was 20 μ L. The molecular weights of the liquefied products were calculated based on the molecular weight of polystyrene standard reagent.

The weight average molecular weight (Mw) and the polydispersity index (Mw/Mn) of the liquefied product were 1532 and 2.0, respectively.

Preparation and characterization for resin

After sodium hydroxide aqueous solution (20 wt%) and formaldehyde solution (36 wt%) were added into the prepared liquefaction products, the mixture was heated at (60 ± 2) °C to perform addition reaction for 1 h, followed by increasing the temperature to (85 ± 2) °C to progress condensation reaction for 1 h.

The characteristics of resins, such as viscosity, pH, gelation time, solid content and free formaldehyde content were measured according to JIS K 6807. The molecular weight of the resins was analyzed by gel permeation chromatography (GPC).

Adhesive preparation

In this study, the general composition of the adhesives applied consisted of 100 parts of resin, 3 parts of sodium hydrogen carbonate and about 7 parts of wheat flour filler.

Panel preparation

Lauan veneers (270 mm (L) \times 270 mm (W) \times 1.6 mm (T)) were stored in the conditions at 20 °C and 45% relative humidity (RH) until Lauan veneers contained an equilibrium moisture content. The veneer was laminated into three-ply plywood panels. Two panels were manufactured for each resin system. Both sides of the core veneers were spread with about 180 g/m² of adhesive. The veneers were mounted immediately after the adhesive was spread. The panels were prepressed at 0.98 MPa for 15 min at a room temperature, and then were pressed at 0.98 MPa at 135 °C for 4 min.

Shear strength and formaldehyde emission tests

Ten specimens (150 mm (L) \times 50 mm (W) \times 1.6 mm (T)) for the measurement of formaldehyde emission and eighteen specimens (80 mm (L) \times 25 mm (W) \times 1.6 mm (T)) for the shear strength test were cut from two panels.

Results and discussion

Behavior of formaldehyde during resin synthesis

Majority of formaldehyde is quickly consumed at early 30 min (Fig. 1). Then, the amount of free formaldehyde decreases gradually to 0.31%. During resin preparation, the added formaldehyde reacts not only with the phenol which remained after liquefaction, but also with the liquefied wood components, particularly lower-molecular-weight cellulose

and lignin, having -OH groups. It is known that wood is mainly composed of cellulose, hemicellulose and lignin. Cellulose is the most inaccessible fraction during wood liquefaction in the presence of phenol. Compared with cellulose, hemicellulose and lignin are easily liquefied. The autohydrolysis and delignification of wood were also reported in the presence of phenol at elevated temperatures. Intramolecular bonds of lignin were partly broken and at the same time, a certain amount of phenol could be introduced into the lignin molecule, especially, at the α -position on the side-chain. During the phenolation process of wood or lignin, the ether linkages in the lignin side-chain were cleaved, producing a phenol derivative of lignin. Phenolysis of lignin side-chains could be followed by the exchange reactions between phenol and the non-condensed nuclei of lignins. As a result, the phenol was linked to the lignin by a carbon-carbon linkage at its ortho or para positions to a phenolic hydroxy group (Maldas *et al.* 1997). On the whole, wood components were subjected to decomposition, phenolation and recondensation. These three reactions dominated the whole liquefaction dynamic process and determined the structural characteristics of liquefied wood (Lin *et al.* 1997). All these factors contributed to the existence of function groups in liquefaction products. During the initial stage, there were many function groups including free phenol that could react with formaldehyde, resulting in the abrupt decrease of formaldehyde. When the reaction are continued, these function groups are gradually consumed, and the content of free formaldehyde decreases gradually.

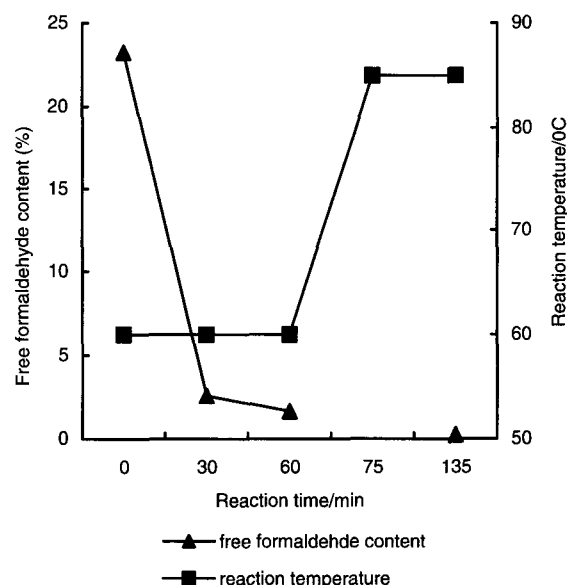


Fig. 1 Relationship between reaction time and free formaldehyde content (resin PF 1.5)

Resin characterization

As shown in Table 1, the solid contents, free formaldehydes, Mw and Mw/Mn of PWF were in the narrow range. And their pH values and gel times also did not change sig-

nificantly with the increasing of F/P molar ratio except for PF1.2 (the molar ratio of formaldehyde to phenol was 1.2). It is also widely accepted that the curing rate of phenolic resins accelerates at alkaline medium. This occurs as the function of phenolic nuclei as a nucleophile is strengthened by ionization of the phenol to form phenate ions. So it is considered that lower pH value is the main reason that gel time of PF1.2 is longer. It is known that the viscosities of phenolic resins from liquefied wood are usually higher than

that of commercial PF. But the fluidities of resins could be improved when the molar ratios of F to P were enhanced as shown in Table 1. In general, there is a reverse relationship between gel time and molecular weight. That is to say, the higher the molecular weights of resins, the shorter their gel times. It is probable that the lower activities of phenolated wood-based PF resins result in the prolonged gel time, although they have higher molecular weights.

Table 1. Properties of PWF and commercial PF resin

Resin	F/P (molar ratio ¹)	Viscosity /MPa·s ⁻¹ (25 °C)	Solid content (%)	pH	Gel time /s	Free formaldehyde (%)	Mw	Mw/Mn
PF 1.2	1.2	2450	41.6	10.07	1020	0.23	708	1.48
PF 1.5	1.5	950	40.2	10.97	658	0.31	686	1.46
PF 1.8	1.8	1002	41.0	11.29	635	0.25	774	1.49
PF 2.1	2.1	740	39.3	11.18	559	0.19	607	1.24
PF 2.4	2.4	440	42.5	11.14	603	0.44	612	1.23
Co PF ²	---	760	44.7	11.12	509	0.41	548	1.16

Notes: ¹ F/P molar ratio--- P stands for the initial phenol mol input at the wood liquefaction stage. ² Co PF---- commercial PF resin.

It should be noticed that the percentage of free formaldehyde was always low, regardless of the amount of added formaldehyde. It is natural that the formaldehyde reacts with the remaining free phenol, but the concentration of free phenol in the liquefied products is no more than 10.15%. Therefore, it can be concluded that the added formaldehyde reacts with not only the residual phenol after liquefaction, but also the phenolated wood components.

As shown in Table 1, The Mw values and Mw/Mn values of PWF were higher than those of commercial PF resin. As far as wood liquefaction is concerned, the three main wood components (cellulose, hemicellulose and lignin) undergo decomposition, phenolation and recondensation. So the liquefaction products are complex mixtures. On the other hand, compared with conventional phenol-formaldehyde condensation reactions, the reactions during the preparation of PWF are more complex. This led to the higher polydispersities of PWF

Plywood bond evaluation

The test results of both shear strength and wood failure for the plywood bonded with PWF and commercial PF resin are illustrated in Fig. 2 and 3, respectively. All the dry shear strengths of plywood exceeded that of the Japan Agriculture Standard (JAS) criteria (0.68MPa) in Fig. 2. After steaming treatment, however, only the shear strengths of plywood bonded with PWF from high molar ratios of F to P (i.e. molar ratio of F to P is over 1.8) met the JAS criteria (JAS SE-1). The results suggested the resins with higher formaldehyde content had better heat and water resistance. It is known that Resols are obtained as a result of alkaline catalyst and an excess of formaldehyde. In the initial stage, the formaldehyde attacked on the phenol and then substitution reaction occurred. The substitution reaction is faster than the subsequent condensation reaction. Consequently,

phenolic alcohols are the predominant intermediate compounds that contain reactive methylol groups. Heating causes the reactive molecules to condense to form large molecules without the addition of a hardener (Pizza 1983). During this procedure, formaldehyde plays an important role and can be only successfully obtained by excess formaldehyde.

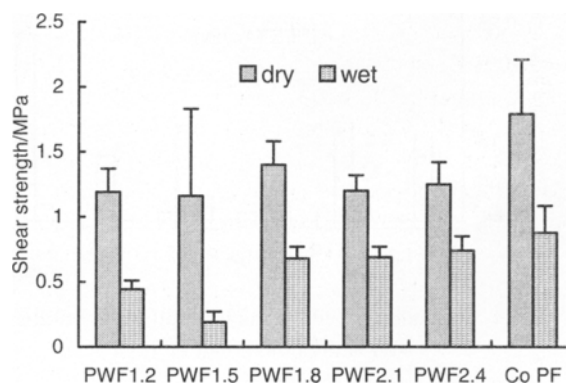


Fig. 2 Shear strength of the plywood bonded with PWF and commercial PF resins

As shown in Fig. 3, although the shear strengths of plywood bonded with PWF were satisfying, the wood failure results were always much lower than that of commercial PF. Most possible explanation is that formaldehyde content in the PWF is much less than that in the commercial resin.

The formaldehyde emissions from the plywoods glued with PWF were quite lower than the reference value of JAS F (F-4 star), (0.3 mg/L) in (Fig. 4). Compared with commercial PF resin, PWF adhesives had the lower formaldehyde emission.

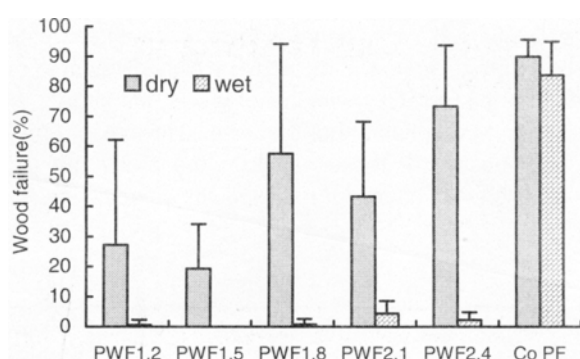


Fig. 3 Wood failure of the plywood bonded with PWF and commercial PF resins

With the ever-increasing demand for healthy wood products, VOCs (volatile organic compound) become an interest of the wood composite industry. Therefore, the emissions of acetaldehyde and acetone were also measured by using a DNPH-HPLC technique (Tohmura *et al.* 2003) in this research. As shown in Fig. 4, the results demonstrated that the PWF adhesives in this study were environmental harmonized products.

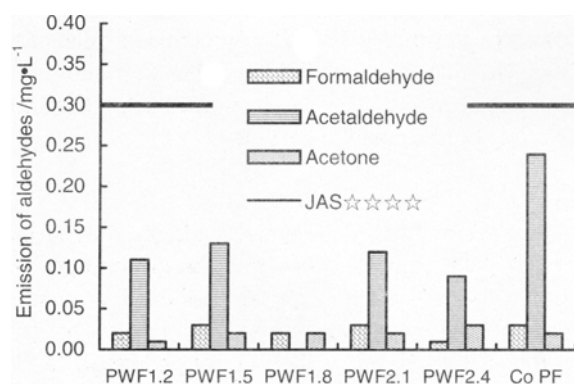


Fig. 4 Emission of aldehydes from plywood bonded with PWF and commercial PF resins

Conclusions

Wood was liquefied at weight ratio of wood to phenol for 0.7. The phenolic adhesives were successfully prepared

from the liquefaction products. When the molar ratio of F to P was over 1.8, both the dry and wet shear strengths of plywood bonded with PWF adhesives met the JAS criteria. The PWF adhesives had high bond quality and bond durability, and their aldehydes emissions were proved to be extremely low.

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